

# PATENT ABSTRACTS OF JAPAN

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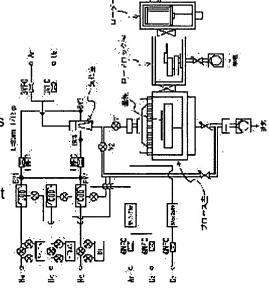
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## (54) METHOD OF CAUSING CVD THIN FILM FOR DEPOSITION

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method of causing CVD thin film to be deposited by which a vaporizer can be used for a long period, without causing clogging, etc., and in addition, a raw material can be supplied stably to a reaction section.

SOLUTION: In this method, a prescribed CVD thin film is formed by making a CVD raw material solution and a gas flow to a CVD chamber for an appropriate period of time through the vaporizer. In this method, only a solvent capable of dissolving deposits adhering to the vaporizer is made to flow to the vaporizer, by switching the gas from the outlet of the vaporizer to gas the evacuation side, after the prescribed period of time has elapsed.



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## **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of CVD thin film deposition of MOCVD etc.

[0002]

[Description of the Prior Art] In development of DRAM, the storage capacitance accompanying detailed-izing poses a problem. From points, such as a soft error, since a front generation and this front extent are required, the KYABASHI wardrobe needs a certain cure. As this cure, the spacial configuration by which that whose cellular structure to 1M was planar structure is called stack structure and trench structure from 4M was taken in, and drawing came the increment in capacitor area. Moreover, the film (this film by which the laminating was carried out is said to - \*\* as ON film.) which carries out the laminating of the thermal oxidation film and the CVD nitride also for a dielectric film on [ the thermal oxidation film of Substrate Si to ] Pori Si was adopted. At 16MDRAM, in order to make the area which contributes to capacity further increase, in the stack mold, the solid mold using a side face, the fin mold also using the rear face of a plate, etc. were taken in.

[0003] However, in such a spacial configuration, lowering of the yield by the increment in the routing counter by complication of a process and buildup of a level difference is regarded as questionable, and implementation after 256 M bit is made difficult. Therefore, as one path for making a degree of integration increase further, without changing the structure of current DRAM, the approach of changing the dielectric of capacitance to the thing of a high dielectric constant was invented. And the thin film of a high dielectric constant single metal paraelectrics oxide attracted attention to Ta 2O5, Y2O3, HfO2, etc. first as a dielectric thin film with a high dielectric constant. For Ta 2O5, 28 and Y2O3 are [ 16 and HfO2 ] about 24, and each specific inductive capacity is 4 to 7 times SiO2.

[0004] However, solid KYABASHITA structure is required for application after 256MDRAMs. It has specific inductive capacity still higher than these oxides, and three kinds, TiO (BaxSr 1-x)3, Pb(ZryTi1-y) O3, and O(ZrbTi(PbaL1-a)1-b) 3, are seen as a hopeful as an ingredient with which application to DRAM is expected. Moreover, the layer structure with the crystal structure very just like a superconducting material of Bi system has a high dielectric constant, has self-polarization of a ferroelectric property, and attracts attention greatly from the point of excelling as a nonvolatile memory in recent years.

[0005] general -- that SrBi2TaO9 ferroelectric thin film formation is practical and promising MOCVD (organic metal vapor growth) -- it is carried out by law.

[0006] The raw materials of a ferroelectric thin film are three kinds of organometallic complexes Sr (DPM)2, Bi (C6H5)3, and Ta (OC2H5)5, are melted to the solvent of THF (tetrahydrofuran), and a hexane and others, respectively, and are used as a raw material solution. Sr (Ta6 (OEt))2 and Bi (OtAm) 3 are also melted to the solvent of a hexane and others, and are used as a raw material solution. In addition, DPM is the abbreviation for JIBIBAROI methane.

[0007] Each material property is shown in a table 1.

[0008]
[A table 1] The property of the raw material of a ferroelectric thin film

| ·   | 沸点(℃)/<br>圧力(mmHg) | 融点(℃) |
|---|--------------------|-------|
| Sr (DPM) <sub>2</sub>                             | 231/0.1            | 210   |
| Bi (Co H <sub>5</sub> ) <sub>3</sub>              | 130/0.1            | 80    |
| Ta (OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> | 118/0.1            | 2 2   |
| THE   | 6 7                | -109  |
| Sr (Ta (OEt) <sub>6</sub> ) <sub>2</sub>          | 176/0.1            | 130   |
| Bi (OtAm) <sub>3</sub>                            | 87/0.1             | 9 0   |

[0009] The equipment used for the MOCVD method is constituted [oxidizer] from a feed zone supplied to the reaction section by gaseous phase reaction and the reaction section which makes membranes form by carrying out surface reaction, and the SrBi2TaO9 thin-film raw material list in a SrBi2TaO9 thin-film raw material.

[0010] And the carburetor for a feed zone to make a thin film raw material evaporating is prepared. [0011] Conventionally, as a technique about a carburetor, the all directions method shown in <u>drawing 16</u> is learned. It is the approach of evaporating by introducing the raw material solution heated by predetermined temperature into the metal filter used the making the touch area of the gas and SrBi2TaO9 ferroelectric thin film raw material solution which are called a metal filter type and exist in a perimeter increase object which is shown in <u>drawing 16</u> (a).

[0012] However, in this technique, since a metal filter starts blinding by evaporation of several hours, it has the problem that a long-term activity cannot be borne, this invention person surmised that the cause was for heating a solution and evaporating from what has low evaporation temperature.

[0013] <u>Drawing 16</u> (b) is the technique of putting the pressure of 30 kgf/cm2 on a raw material solution, making a raw material solution emitting from 10-micrometer pore, and making a raw material solution evaporating by expansion.

[0014] However, in this technique, pore is got blocked by the activity of several hours, and it has the problem that a long-term activity cannot be borne too.

[0015] Moreover, when a raw material solution is the mixed solution of two or more organometallic complexes, for example, the mixed solution of Sr (DPM)2/THF, Bi (C6H5)3/THF, and Ta (OC2H5) 5/THF, and evaporates this mixed solution with heating, the highest solvent (THF in this case) of vapor pressure evaporates promptly, and in order that an organometallic complex may carry out deposit adhesion on a heating surface, the problem that stable feeding to the reaction section is not made arises. The heating value from which all of these approaches shown in drawing 1 are set in a liquid or the Myst condition, and a solvent may evaporate or change will be applied.

[0016] Furthermore, in MOCVD, in order to obtain the film excellent in homogeneity, it is requested that the evaporation gas which the raw material solution distributed to homogeneity should be obtained. However, with the above-mentioned conventional technique, it can not necessarily be finishing responding to this request.

[0017] \*\* or the request to cut -- it should respond -- this invention person -- separately -- a degree -- the technique is offered.

[0018] Namely, the gas inlet for introducing the gas passageway formed in the interior of \*\*, and the carrier gas pressurized by this gas passageway as shown in <u>drawing 15</u>, The means for supplying a raw material solution to this gas passageway, and the gas outlet for sending the carrier gas containing a raw material solution to the evaporation section, The distributed section which has a means for cooling this

gas passageway, and the radiant heat prevention blowout section in which heat energy does not join material gas in the distributed department with the radiant heat from the evaporation section, and which was cooled like;

\*\* It is the carburetor for MOCVD which had the vaporizing tube by which the end was connected to the coil of an MOCVD system and the other end was connected to said gas outlet, and the heating means for heating this vaporizing tube, and has been sent from said distributed section and which has the business on which heat energy does not join material gas in the distributed department with the radiant heat from the evaporation section and; evaporation section for making the carrier gas containing a raw material solution heat and evaporate.

[0019] Compared with the former, this technique has very little blinding and is a carburetor for MOCVD in which a long-term activity is possible and in which the stable feeding to the reaction section is possible.

[0020] Moreover, the inlet of oxygen where this technique was heated beforehand is established in the evaporation section lower stream of a river.

[0021] However, also with this technique, a deposit of a crystal is found at the path of gas and blinding may still arise.

[0022] Moreover, in the formed film, the carbon (30 - 40at%) of a large quantity contains. In order to remove this carbon, the need of performing annealing in the elevated temperature after membrane formation (example: 800 degrees C, 60 minutes, oxygen ambient atmosphere) will arise.

[0023] When forming membranes furthermore, the variation in a presentation ratio will arise greatly. [0024]

[Problem(s) to be Solved by the Invention] This invention does not start blinding etc., and a long-term activity is possible and it aims at offering the approach of \*\* CVD thin film deposition. [0025]

[Means for Solving the Problem] This invention is the approach of the CVD thin film deposition characterized by pouring only the solvent (henceforth a "cleaning solvent") which may dissolve the affix which changed the gas from a carburetor outlet to the exhaust side, and adhered to the carburetor to this carburetor, when this predetermined time amount passes a CVD raw material solution and gas via a carburetor in the suitable CVD thin film deposition approach for a CVD chamber which carries out a time amount style and forms a predetermined CVD thin film.

[0026] This invention is [0027] while changing the gas from a carburetor outlet to an exhaust side, pouring to a carburetor only the solvent which may dissolve the affix adhering to a carburetor and cleaning a carburetor, if this predetermined time amount passes a CVD raw material solution and gas via a carburetor in the suitable CVD thin film deposition approach for a CVD chamber which carries out a time amount style and forms a predetermined CVD thin film. It is the approach of the CVD thin film deposition characterized by doing the activity which throws into ejection the substrate which formed the predetermined thin film in parallel to the time of performing the above-mentioned cleaning in a CVD chamber, and throws a still newer substrate into a CVD chamber.

[0028] This invention sets a CVD raw material solution and gas via a carburetor to the suitable CVD thin film deposition approach for a CVD chamber which carries out a time amount style and forms a predetermined CVD thin film. If predetermined time amount passes, while changing the gas from a carburetor outlet to an exhaust side and interrupting thin film deposition It changes into the class and flow rate of a new CVD raw material solution. The sum (volume) of a new CVD raw material solution flow rate 1 time of piping capacity until it results in a carburetor from a CVD raw material solution change bulb Or if twice is exceeded, a new CVD raw material solution and gas are gone via a carburetor. It is the approach of the CVD thin film deposition characterized by forming two sorts of suitable CVD thin films for a CVD chamber with which a time amount style is carried out, thin film deposition is resumed, and presentations differ.

[0029] This invention sets a CVD raw material solution and gas via a carburetor to the suitable CVD thin film deposition approach for a CVD chamber which carries out a time amount style and forms a predetermined CVD thin film. If predetermined time amount passes, while changing the gas from a

carburetor outlet to an exhaust side and interrupting thin film deposition It changes into the class and flow rate of a new CVD raw material solution promptly. The 1st actuation and the sum (volume) of a new CVD raw material solution flow rate 1 time of piping capacity until it results in a carburetor from a CVD raw material solution change bulb Or if twice is exceeded, a new CVD raw material solution and gas are gone via a carburetor. It is the approach of the CVD thin film deposition characterized by repeating the 2nd actuation which forms the suitable CVD thin film of \*\* the 2nd from which a time amount style is carried out, thin film deposition is resumed, and a presentation differs for a CVD chamber, and forming two or more sorts of CVD thin films continuously.

[0030] This invention sets a CVD raw material solution and gas via a carburetor to the suitable CVD thin film deposition are sorted for a CVD chamber which carries out a time amount style and forms a

[0030] This invention sets a CVD raw material solution and gas via a carburetor to the suitable CVD thin film deposition approach for a CVD chamber which carries out a time amount style and forms a predetermined CVD thin film. If predetermined time amount passes, while changing the gas from a carburetor outlet to an exhaust side and interrupting thin film deposition Change into the class and flow rate of a new CVD raw material solution promptly, and substrate temperature and reaction pressure are changed further. I time of piping capacity until the sum (volume) of a new CVD raw material solution flow rate results in a carburetor from a CVD raw material solution change bulb Or if twice is exceeded, a new CVD raw material solution and gas are gone via a carburetor. It is the approach of the CVD thin film deposition characterized by repeating the 2nd actuation which forms the suitable CVD thin film of \*\* the 2nd from which a time amount style is carried out, thin film deposition is resumed, and a presentation differs for a CVD chamber, and forming two or more sorts of CVD thin films continuously.

[0031] As for said cleaning solvent, it is desirable that it is the solvent of a CVD raw material. It can clean only by the change of a bulb, without preparing a new cleaning solvent. As for said cleaning solvent, it is desirable that they are one or more sorts of a hexane, benzene, toluene, an octane, and Deccan. These chemicals become possible [ preventing the blinding of the carburetor in MOCVD easily ].

[0032] \*\*\*\* which can do piping capacity from a CVD raw material solution change bulb to a carburetor -- lessening is desirable. For example, it is desirable to design, as shown in ZU 26 and ZU 27.

[0033] When the flow rate of a cleaning solvent is especially made into (Xcc/min.), it is desirable to be referred to as 8 or less Xccs, it is more desirable to be referred to as 2 or less Xccs, and carrying out to below Xcc is still more desirable. By considering as this range, it can change very promptly. [0034] The carburetor in this invention is the distributed section which has the gas inlet for introducing carrier gas into the gas passageway formed in the interior of \*\*, and this gas passageway, the means for supplying a raw material solution to this gas passageway, a gas outlet for sending the carrier gas containing a raw material solution to the evaporation section, and a means for cooling this gas passageway.;

- \*\* Carry out having prepared the radiation prevention section which has the vaporizing tube by which the end was connected to the reaction section of the various equipments of membrane formation and others, and the other end was connected to said gas outlet, and a heating means for heating this vaporizing tube, has the evaporation section for making the carrier gas containing the atomized raw material solution which has been sent from said distributed section heat and evaporate, and;, and has pore on the outside of this gas outlet as the description. The carburetor of this invention is the distributed section which has the gas inlet for introducing the gas passageway formed in the interior of \*\*, and the carrier gas pressurized by this gas passageway, a means for supplying a raw material solution to this gas passageway, and a gas outlet for sending the carrier gas containing a raw material solution to the evaporation section.;
- \*\* The vaporizing tube by which the end was connected to the reaction section of the various equipments of membrane formation and others, and the other end was connected to said gas outlet, It has a heating means for heating this vaporizing tube, and has the evaporation section for making the carrier gas containing the raw material solution sent from said distributed section heat and evaporate, and;. The \*\* aforementioned distribution section It has the rod which has a cylindrical or outer diameter smaller

than the bore of a cone-like centrum. cylindrical or the distributed section body which has a cone-like centrum -- this -- this rod It is inserted in cylindrical or a cone-like centrum. the carburetor side of the periphery -- 1 or 2 or more spiral slots -- having -- and -- this -- \*\* What is characterized by preparing the cooled radiation prevention section in which it has pore in a gas outlet side, and a bore spreads in the shape of a taper toward a carburetor side in the outside of this gas outlet is suitable.

[0035] The carburetor in this invention is the distributed section which has the gas inlet for introducing a carrier into the gas passageway formed in the interior of \*\*, and this gas passageway, the means for supplying a raw material solution to this gas passageway, a gas outlet for sending the carrier gas containing a raw material solution to the evaporation section, and a means for cooling this gas passageway.;

- \*\* The vaporizing tube by which the end was connected to the reaction section of the various equipments of membrane formation and others, and the other end was connected to said gas outlet, It has a heating means for heating this vaporizing tube, and has the evaporation section for making the carrier gas containing the raw material solution sent from said distributed section heat and evaporate, and;. As carrier gas from said gas inlet What is characterized by enabling it to introduce a oxidizing gas or its mixed gas is more suitable than the approach of adding and introducing few oxidizing gases into Ar or N2, helium, etc., or primary oxygen supply opening of the blowout section latest.

  [0036] The carburetor in this invention is the distributed section which has the gas inlet for introducing a carrier into the gas passageway formed in the interior of \*\*, and this gas passageway, the means for supplying a raw material solution to this gas passageway, a gas outlet for sending the carrier gas containing a raw material solution to the evaporation section, and a means for cooling this gas passageway.;
- \*\* The vaporizing tube by which the end was connected to the reaction section of the various equipments of membrane formation and others, and the other end was connected to said gas outlet, Had the heating means for heating this vaporizing tube, and have been sent from said distributed section. It has the evaporation section for making the carrier gas containing a raw material solution heat and evaporate, and;, the radiation prevention section which has pore is prepared in the outside of this gas outlet, and what is characterized by enabling it to introduce carrier gas and a oxidizing gas from said gas inlet is used suitably.

[0037] What is made to shear and atomize this raw material solution, considers as material gas, and is characterized by to make oxygen contain in carrier gas in the evaporation approach of making this material gas supplying and evaporating, subsequently to the evaporation section is suitable for the evaporation approach in this invention by making a gas passageway inject high-speed carrier gas towards the raw material solution which introduced the raw material solution and was this introduced. [0038] The mixed section which mixes two or more raw material solutions supplied from two or more solution paths to which the carburetor in this invention supplies a raw material solution, and these two or more solution paths, In the mixed raw material solution which came out of this mixed section in the supply path which has the outlet where an end is open for free passage in the mixed section, and becomes an evaporation section side, and this supply path, carrier gas Or what is characterized by forming the gas passageway arranged so that the mixed gas of carrier gas and oxygen may be sprayed, the cooling means for cooling this supply path, and \*\* is suitable.

[0039] Two or more solution paths to which the distributed machine in the above-mentioned carburetor supplies a raw material solution, [in the mixed section which mixes two or more raw material solutions supplied from these two or more solution paths, the supply path which has the outlet where an end is open for free passage in the mixed section, and becomes an evaporation section side, and this supply path ] In the mixed raw material solution which came out of this mixed section, carrier gas Or the gas passageway arranged so that the mixed gas of carrier gas and oxygen may be sprayed, The cooling means for cooling this supply path, and the distributed machine with which \*\* is formed, The vaporizing tube by which the end was connected to the reaction section of the various equipments of membrane formation and others, and the other end was connected to the outlet of said distributed machine, What is characterized by preparing the radiation prevention section which has a heating means

for heating this vaporizing tube, has the evaporation section for making the carrier gas containing the raw material solution sent from said distributed section heat and evaporate and;, and has pore on the outside of this outlet is suitable.

[0040]

[Example] (Example 1) The carburetor for MOCVD applied to an example 1 at <u>drawing 1</u> is shown. [0041] The gas passageway 2 formed in the interior of the distributed section body 1 which constitutes the distributed section from this example, The gas inlet 4 for introducing the carrier gas 3 pressurized by the gas passageway 2, The means 6 for supplying the raw material solution 5 to the carrier gas which passes a gas passageway 2, and Myst-izing the raw material solution 5 (feeding hole), The gas outlet 7 for sending the carrier gas (material gas) containing the Myst-ized raw material solution 5 to the evaporation section 22, The means 18 for cooling the carrier gas which flows the inside of a gas passageway 2 (cooling water), The distributed section 8 which \*\*\*\*, and the vaporizing tube 20 by which the end was connected to the coil of an MOCVD system and the other end was connected to the gas outlet 7 of the distributed section 8, It has the heating means (heater) 21 for heating a vaporizing tube 20, and has the evaporation section 22 for making the carrier gas with which the raw material solution sent from said distributed section 8 was distributed heat and evaporate, and the radiation prevention section 102 which has pore 101 is formed in the outside of a gas outlet 7.

[0042] An example is explained more to a detail below. In the example shown in drawing, the interior of the distributed section body 1 is a cylinder-like centrum. The rod 10 is inserted in these hollow circles, and the gas passageway 2 is formed with the wall and rod 10 of a distributed section body. In addition, not only the shape of a cylinder but other configurations are sufficient as a centrum. For example, the shape of a cone is desirable. As an include angle of \*\*\*\* of a conic centrum, 0-45 degrees is desirable and 8-20 degrees is more desirable. Also in other examples, it is the same.

[0043] In addition, as for the cross section of a gas passageway, 2 is desirable 0.10-0.5mm. Processing is difficult at less than [0.10mm] two. If 2 is exceeded 0.5mm, in order to accelerate carrier gas, the \*\*\*\* need for large flow rates will produce high-pressure carrier gas. If the carrier gas of a large flow rate is used, in order to maintain a reaction chamber to reduced pressure (example: 1.0Torr), a mass large-sized vacuum pump is needed. Since it is difficult, in order to attain industrial utilization, as for adoption of the vacuum pump with which a displacement exceeds 10,000l. / min. (at, 1.0Torr), 2 is desirable the proper flow rate of 0.10-0.5mm, i.e., gas-passageway area.

[0044] The gas inlet 4 is established in the end of this gas passageway 2. The source (not shown) of carrier gas (for example, N2, Ar, helium) is connected to the gas inlet 4.

[0045] Mostly, a gas passageway 2 is made open for free passage, the feeding hole 6 is formed, the raw material solution 5 can be introduced into a gas passageway 2, the carrier gas of the distributed section body 1 which passes a gas passageway 2 for the raw material solution 5 can be made to be able to distribute the raw material solution 5 to a central flank, and it can consider as material gas at it. [0046] The gas outlet 7 which is open for free passage to the vaporizing tube 20 of the evaporation section 22 is established in the end of a gas passageway 2.

[0047] The space 11 for pouring cooling water 18 is formed in the distributed section body 1, and the carrier gas which flows the inside of a gas passageway 2 is cooled by pouring cooling water 8 in this space. Or a Peltier device etc. may be installed instead of this space, and you may cool. Evaporation of only a solvent will produce the inside of the gas passageway 2 of the distributed section 8, without simultaneous evaporation with the solvent of a raw material solution and an organometallic complex arising in a gas passageway 2, in order to receive the thermal effect at the heater 21 of the evaporation section 22. Then, evaporation of only a solvent is prevented by cooling the carrier gas with which it flowed and the \*\*\*\* raw material solution distributed the inside of a gas passageway 2. Especially, cooling of the downstream is more important than the feeding hole 6, and the downstream of the feeding hole 6 is cooled at least. Cooling temperature is the temperature below the boiling point of a solvent. For example, in THF, it is 67 degrees C or less. Especially, the temperature in a gas outlet 7 is important. [0048] In this example, the radiation prevention section 102 which has pore 101 is further formed in the outside of a gas outlet 7. In addition, 103,104 is seal members, such as an O ring. What is necessary is

for Teflon (trademark), stainless steel, a ceramic, etc. just to constitute this radiation prevention section 102. Moreover, constituting with the thermally conductive outstanding ingredient is desirable. [0049] According to this invention person's knowledge, in the conventional technique, the heat in the evaporation section will mind a gas outlet 7 as radiant heat, and will overheat the gas in a gas passageway 2. Therefore, even if it cools with cooling water 18, the low-melt point point component in gas will deposit in about seven gas outlet.

[0050] The radiation prevention section is a member for preventing that this radiant heat spreads in gas. Therefore, as for the cross section of pore 101, it is desirable to make it smaller than the cross section of a gas passageway 2. It is desirable to carry out to 1/2 or less, and it is more desirable to carry out to 1/3 or less. Moreover, it is desirable to micrify pore. It is desirable to micrify in the dimension from which the gas flow rate spouted especially turns into subsonic.

[0051] Moreover, as for the die length of said pore, it is desirable that they are 5 or more times of said pore dimension, and it is more desirable that they are 10 or more times.

[0052] Moreover, the lock out by the carbide in a gas passageway (especially gas outlet) is not produced to the activity broken at a long period of time by cooling the distributed section.

[0053] The distributed section body 1 is connected to the vaporizing tube 20 in the downstream of the distributed section body 1. Connection between the distributed section body 1 and a vaporizing tube 20 is made by the joint 24, and this part serves as a connection 23.

[0054] General drawing is shown in <u>drawing 2</u>. The evaporation section 22 consists of a vaporizing tube 20 and a heating means (heater) 21. A heater 21 is a heater for making the carrier gas with which the flowing raw material solution distributed the inside of a vaporizing tube 20 heat and evaporate. Since the method of using a liquid and a gas with large heat capacity for a heat carrier was most excellent as a heater 21 in order to have heated so that it might become uniform temperature to the die-length direction of a vaporizing tube although constituted by sticking a cylindrical heater and a mantle heater on the periphery of a vaporizing tube 20 conventionally, this was adopted.

[0055] As a vaporizing tube 20, it is desirable to use stainless steel, such as SUS316L, for example. Although it should just be decided suitably that the temperature of evaporation gas will be the die length fully heated, when evaporating SrBi2Ta2O9 raw-material solution 0.04ccm, the thing of the outer diameter of 3/4 inch and 100mm of die-length numbers should just be used for the dimension of a vaporizing tube 20, for example.

[0056] Although the downstream edge of a vaporizing tube 20 is connected to the coil of an MOCVD system, the oxygen supply opening 25 is formed in the vaporizing tube 20 as an oxygen supply means, and it enables it to have mixed in carrier gas the oxygen heated by predetermined temperature in this example.

[0057] First, \*\*\*\* of the raw material solution to a carburetor is described. As shown in <u>drawing 3</u>, reserve tanks 32a, 32b, 32c, and 32d are connected to the feeding opening 6 through massflow controllers 30a, 30b, 30c, and 30d and Bulbs 31a, 31b, 31c, and 31d, respectively.

[0058] Moreover, it connects with the carrier gas bomb 33 at each reserve tank 32a, 32b, 32c, and 32d. [0059] The detail of a reserve tank is shown in <u>drawing 4</u>.

[0060] The reserve tank is filled up with the raw material solution, and it is each reservoir tank (the carrier gas (for example, inert gas Ar, helium, and Ne) of 1.0 - 3.0 kgf/cm2 is sent into 300 cc of content volume, and the product made from SUS.). Since the inside of a reserve tank is pressurized by carrier gas, the inside of tubing of the side which is in contact with the solution can be pushed up, even the massflow controller for liquids (the product made from STEC, full-scale flow rate 0.2 cc/min) is fed, a flow rate is controlled here, and a raw material solution is conveyed to the feeding hole 6 from the feeding inlet port 29 of a carburetor.

[0061] It is conveyed to the reaction section by the carrier gas controlled by the massflow controller by constant flow. It is a massflow controller (the product made from STEC and the oxygen (oxidizer) controlled by full-scale flow rate 2 L/min by the amount of - steady flow are also conveyed to the reaction section.) simultaneously.

[0062] Since the raw material solution is dissolving the liquid or the solid-state-like organometallic

complex in the solvent of THF which is a solvent, and others in ordinary temperature, if it is left as it is, by evaporation of a THF solvent, an organometallic complex will deposit and it will become solid-like eventually. Therefore, it is assumed that the inside of piping in contact with an undiluted solution produces lock out of piping etc. by this. Therefore, in order to control lock out of piping, it thinks that what is necessary is for the solvent of THF and others just to wash the inside of piping after membrane formation activity termination, and a carburetor, and the washing line is prepared. Also including a raw material container exchange activity, washing considers as the section to a carburetor from a container outlet side, and flushes with a solvent the part which suited each activity.

[0063] Bulbs 31b, 31c, and 31d were made open, and carrier gas was fed in reserve tanks 32b and 32c and 32d. Even a massflow controller (full-scale flow rate made from STEC 0.2 cc/min) is fed, a flow rate is controlled here, and a solution raw material is conveyed to a raw material solution by the feeding hole 6 of a carburetor.

[0064] On the other hand, carrier gas was introduced from the gas inlet of a carburetor. As for the maximum pressure by the side of a feed hopper, it is desirable to consider as two or less 3 kgf/cm, the maximum stream flows which can pass are about 1200 cc/min at this time, and the passage rate of flow of a gas passageway 2 is attained up to 100 and dozens m/s.

[0065] If a raw material solution introduces the gas passageway 2 of a carburetor into the flowing carrier gas from the feeding hole 6, a raw material solution will be sheared by the high-speed style of carrier gas, and will be ultrafine-particle-ized. As a result, a raw material solution is distributed in the state of an ultrafine particle in carrier gas. The carrier gas (material gas) which the raw material solution distributed in the state of the ultrafine particle is atomized and emitted to the evaporation section 22 with a high speed. The include angle which a gas passageway and a feeding hole form is optimized. A solution is lengthened by gas when carrier passage and a raw material solution inlet are acute angles (30 degrees). A solution will be pushed on gas if it is 90 degrees or more. The optimal include angle is decided from the viscosity and the flow rate of a solution. When viscosity and a flow rate are large, a solution flows smoothly by making it an acute angle more. When using a hexane for a solvent and forming the SBT film, since viscosity and a flow rate are small, about 84 degrees is desirable. [0066] Three sorts of raw material solutions controlled by constant flow flow into a gas passageway 2 from the feeding hole 6 through each feeding inlet port 29, and after they move a gas passageway with the carrier gas used as a high-speed flow, they are emitted to the evaporation section 22. Also in the distributed section 8, since it is heated by the heat from the evaporation section 22 and evaporation of solvents, such as THF, is promoted, a raw material solution cools the section from the feeding inlet port 29 to the feeding hole 6, and the section of a gas passageway 2 with the refrigerant of water and others. [0067] By mixing of the oxygen heated by the predetermined temperature of the oxygen supply opening 25 prepared just before evaporation is promoted and reaching the coil of MOCVD while conveying the vaporizing tube 20 interior heated by predetermined temperature at the heater 21, the raw material solution which was emitted from the distributed section 8 and which was distributed in the shape of a particle in carrier gas serves as a gaseous mixture, and flows into a coil. In addition, this example estimated by replacing with membrane formation and analyzing the reaction gestalt of evaporation gas. [0068] The vacuum pump (not shown) was connected from the exhaust port 42, impurities, such as moisture in a coil 44, were removed by reduced pressure actuation for about 20 minutes, and the bulb 40 of exhaust-port 42 lower stream of a river was closed.

[0069] Cooling water was poured by about 400 cc/min to the carburetor. On the other hand, the bulb 40 was opened, after filling the carrier gas of 3 kgf/cm2 with the sink and filling the inside of a coil 44 with 495 cc/min enough with carrier gas. The temperature in a gas outlet 7 was lower than 67 degrees C. [0070] The section and the gas pack from 200 degrees C and the coil 44 to the gas pack 46 were heated at 100 degrees C, and the inside of a coil 44 was heated for the inside of a vaporizing tube 20 at 300 degrees C - 600 degrees C.

[0071] The inside of a reserve tank was pressurized with carrier gas, and the predetermined liquid was poured with the massflow controller.

[0072] Sr (DPM)2, Bi (C6H5)3, Ta (OC2H5)5, and THF were passed by the flow rate of 0.04 cc/min,

0.08 cc/min, 0.08 cc/min, and 0.2 cc/min, respectively.

[0073] It investigated whether resultants would be collected in the aperture gas pack 46, the bulb in front of the 20-minute blasting-fumes pack 46 would be analyzed in a gas chromatograph, and the detected product and the product in the reaction formula which inquired based on the reaction theory would be in agreement. Consequently, in this example, the detected product and the product in the reaction formula examined based on the reaction theory were well in agreement.

[0074] Moreover, the coating weight of the carbide in the outside surface by the side of the gas outlet 7 of the distributed section body 1 was measured. Consequently, the coating weight of carbide was very slight and there was than the case where the equipment shown in <u>drawing 14</u> is used. [still less] [0075] In addition, when the metal used as a film raw material is mixed or dissolved in a solvent and it considers as a raw material solution, as for this raw material solution, it is common that a metal serves as a complex and it will be in a liquid / liquid condition (perfect solvent liquid). However, when this invention person investigated the raw material solution minutely, the metal complex did not become the thing of a scattering molecule condition, but also when the metal complex itself may exist as a particle with a magnitude of 1-100nm and it existed in part as a solid-state / a liquid condition in a solvent, the knowledge of a certain thing was not necessarily carried out. Although it is thought that it is easy to produce especially the blinding at the time of evaporation at the time of the raw material solution of this condition, when the carburetor of this invention is used, blinding is not produced even if it is the case of the raw material solution of this condition.

[0076] Moreover, in the solution which a raw material solution saves, a particle tends to sediment at the pars basilaris ossis occipitalis for the gravity. Then, it is desirable on blinding prevention to produce and cheat out of the convection current in a stock solution, and to carry out homogeneity distribution of the particle by heating a pars basilaris ossis occipitalis (below the vaporization point that is a solvent to the last). Moreover, as for the side face on the top face of a container, cooling is more desirable while heating a pars basilaris ossis occipitalis. Of course, it heats at the temperature below the evaporating temperature of a solvent. In addition, it is desirable that a heating heater sets up thru/or controls so that the heating heating value of a vaporizing tube up field becomes larger than the heating heating value of a downstream region. That is, since the gas by which water cooling was carried out spouts from the distributed section, a heating heating value is enlarged in a vaporizing tube up field, and it is desirable to form the heating heater which sets up or controls a heating heating value small in a downstream region. [0077] (Example 2) The carburetor for MOCVD applied to an example 2 at drawing 5 is shown. [0078] In this example, the cooling water path 106 was formed in the periphery of the radiation prevention section 102, and the cooling means 50 was formed in the periphery of a connection 23, and the radiation prevention section 102 was cooled.

[0079] Moreover, the impression 107 was formed on the outskirts of an outlet of pore 101.

[0080] Other points presupposed that it is the same as that of an example 1.

[0081] In this example, coincidence with the detected product and the product in the reaction formula examined based on the reaction theory better than the case of an example 1 was obtained.

[0082] Moreover, the result of having measured the coating weight of the carbide in the outside surface by the side of the gas outlet 7 of the distributed section body 1 was about 1 in the case of an example 1 / 3 times the coating weight of carbide of this.

[0083] (Example 3) The carburetor for MOCVD applied to an example 3 at <u>drawing 6</u> is shown. [0084] In this example, the taper 51 is formed in the radiation prevention section 102. The Dead Zone of the part is lost for this taper 51, and stagnation of a raw material can be prevented. Other points presupposed that it is the same as that of an example 2.

[0085] In this example, coincidence with the detected product and the product in the reaction formula examined based on the reaction theory better than the case of an example 2 was obtained.
[0086] Moreover, the coating weight of carbide of the result of having measured the coating weight of the carbide in the outside surface by the side of the gas outlet 7 of the distributed section body 1 was

[ that there is nothing ] near.

[0087] (Example 4) The deformation example of a gas passageway is shown in drawing 7.

[0088] In drawing 7 (a), the slot 70 is formed in the front face of a rod 10, and suppose that it is almost the same as that of the bore of the hole which opened the outer diameter of a rod 10 in the interior of the distributed section body 1. therefore -- without it carries out eccentricity only by inserting a rod 10 in a hole -- a rod 10 can be arranged inside. Moreover, it is not necessary to use a screw etc. This slot 70 serves as a gas passageway.

[0089] In addition, although two or more slots 70 may be formed in the longitudinal direction medial axis of a rod 10, and parallel, you may form in the front face of a rod 10 spirally. When spiral, the material gas which was more excellent in homogeneity can be obtained.

[0090] <u>Drawing 7</u> (b) is the example which prepared the mixed section in the point of a rod 10. Suppose that it is almost the same as that of the bore of the hole which opened the biggest path of a point in the interior of the distributed section body 1. The space formed by the rod point and the inner surface of a hole serves as a gas passageway.

[0091] in addition -- although the example shown in (a) and (b) is an example which had processed it on the front face of a rod 10 -- as a rod -- a cross section -- a crevice is established in the direction of a hole using a circular thing, and it cannot be overemphasized that it is good also as a gas passageway. In addition, it is desirable to perform installation of a rod by about seven H7xh6-JS specified to JIS. [0092] (Example 5) An example 5 is explained based on drawing 8.

[0093] The gas inlet 4 for the carburetor for MOCVD of this example to introduce the gas passageway formed in the interior, and the carrier gas 3 pressurized by the gas passageway, The means for supplying the raw material solutions 5a and 5b to a gas passageway, and the gas outlet 7 for sending the carrier gas containing the raw material solutions 5a and 5b to the evaporation section 22, The distributed section 8 which \*\*\*\*, and the vaporizing tube 20 by which the end was connected to the coil of an MOCVD system and the other end was connected to the before gas outlet 7, It has a heating means for heating a vaporizing tube 20, and has the evaporation section 22 for making the carrier gas containing the raw material solution sent from the distributed section 8 heat and evaporate. The distributed section 8 The distributed section body 1 which has a cylindrical centrum, and the rod 10 which has an outer diameter smaller than the bore of a cylindrical centrum, It \*\*\*\*, and has 1 or two or more spiral slots 60 in the carburetor 22 side of the periphery of a rod 10, and a rod 10 is inserted in this cylindrical centrum, it has pore 101 on the outside of a gas outlet 7, and the radiation prevention section 101 in which a bore spreads in the shape of a taper toward a carburetor 22 side is formed in it.

[0094] If the raw material solution 5 is supplied to the gas passageway to which high-speed carrier gas 3 flows, a raw material solution will be sheared and atomized. That is, the raw material solution which is a liquid is sheared by the high-speed style of carrier gas, and is particle-ized. The particle-ized raw material solution is distributed in carrier gas in the state of a particle. This point is the same as an example 1.

[0095] In addition, the following conditions are desirable in order to perform shearing and atomization the optimal.

[0096] It is desirable to perform supply of the raw material solution 5 by 0.005 - 2 cc/min, it is more desirable to carry out by 0.005 - 0.02 c/min, and it is still more desirable to carry out by 0.1 - 0.3 cc/min. When supplying simultaneously two or more raw material solutions (a solvent is included), it is the total amount.

[0097] Moreover, as for carrier gas, it is desirable to supply at the rate of 10 - 200 m/sec, and its 100 - 200 m/sec is more desirable. It is not to choose the passage cross section from which a raw material solution flow rate and a carrier gas flow rate have a correlation, optimal shear and atomization are realized, and ultrafine particle Myst is acquired, and a configuration until it says.

[0098] In this example, since the spiral slot 60 is formed in the periphery of a rod 10 and clearance space exists between the distributed section body 1 and a rod 10, the carrier gas containing the raw material solution which changed into the atomization condition forms a turning style along the spiral slot 60 while going straight on considering this clearance space as a rectilinear-propagation style.

[0099] Thus, this invention person found out distributing uniformly the raw material solution atomized in the condition that a rectilinear-propagation style and a turning style coexist in carrier gas. Although

the reason of whether uniform distribution is obtained by why is not necessarily clear if a rectilinear-propagation style and a turning style coexist, it thinks as follows. By existence of a turning style, a centrifugal force works with flow and secondary flow arises. Mixing of a raw material and carrier gas is promoted by this secondary flow. That is, a-like secondary descendant style arises in the direction of a right angle to flow according to the centrifugal effect of a turning style, and the raw material solution atomized by this is considered that the inside of carrier gas distributes uniformly.

[0100] Hereafter, this example is explained more to a detail.

[0101] It consists of this examples so that four kinds of raw material solutions 5a, 5b, 5c, and 5d (an organic metal raw material and 5d are solvent raw materials, such as THF, for 5a, 5b, and 5c) may be supplied to a gas passageway as an example.

[0102] It atomizes, respectively, and in order to mix the carrier gas (it is called "material gas") containing the raw material solution which became ultrafine particle-like, in this example, the part which does not have a spiral slot in a part for the downstream of the part corresponding to the feeding hole 6 of a rod 10 is prepared. This part serves as the pre mixing section 65. In the pre mixing section 65, it is mixed to some extent and the material gas of three kinds of organic metals turns into perfect mixed material gas in the field of down-stream spiral structure further. In order to obtain uniform mixed material gas, the die length of this mixing section 65 has 5-20 desirablemm, and its 8-15mm is more desirable. When [ this ] out of range, mixed material gas with one kind of high concentration may be sent to the evaporation section 22 among the material gas of three kinds of organic metals.

[0103] In this example, a parallel part 67 and the taper section 58 are formed in the edge 66 of the upstream of a rod 10. The parallel part of the same bore as the outer diameter of a parallel part 67 and the parallel part 67 of a rod 10 corresponding to the taper section 58 and the taper section of the same taper as the taper of a rod 10 are prepared also in the cylinder centrum of the distributed section body 1. Therefore, if a rod 10 is inserted from drawing top left-hand side, a rod 10 will be held at the hollow circles of the distributed section body 1.

[0104] In this example, since the taper is formed and held to the rod 10 unlike the case of an example 1, even if it uses high-pressure carrier gas rather than 3 kgf/cm2, migration of a rod 10 can be prevented. That is, if the maintenance technique shown in <u>drawing 8</u> is adopted, carrier gas can be passed by the pressure of 3kg/cm2 or more. Consequently, the cross section of a gas passageway is made small and supply of high-speed carrier gas is attained more by little gas. That is, supply of the carrier gas of the high speed of 50 - 300 mm/s also becomes possible. It is the same if this maintenance technique is adopted also in other above mentioned examples.

[0105] In addition, as shown in <u>drawing 9</u> (b), Slots 67a, 67b, 67c, and 67d are formed in the part corresponding to the feeding hole 6 of a rod 10 as a path of carrier gas. As the depth of each slots 67a, 67b, 67c, and 67, 0.005-0.1mm is desirable. In less than 0.005mm, the fabricating operation of a slot becomes difficult. Moreover, 0.01-0.05 are more desirable. Generating of blinding etc. is lost by considering as this range. Moreover, a high-speed style is easy to be obtained.

[0106] About maintenance of a rod 10, and formation of a gas passageway, the configuration of the configuration shown in <u>drawing 1</u> in an example 1 and others may be adopted.

[0107] \*\*\*\*\*\* [ slot / two or more / there \*\*\*\*\*\* one spiral slot 60, as shown in <u>drawing 9</u> (a), but ] as shown in <u>drawing 10</u>. Moreover, when forming two or more spiral slots, you may make it cross. When it is made to cross, the material gas distributed more to homogeneity is obtained. However, the gas flow rate to each slot is taken as the cross section from which 10 or more m/sec is obtained.

[0108] It is not limited to especially the dimension and configuration of the spiral slot 60, but the dimension and configuration shown in <u>drawing 9</u> (c) are raised as an example.

[0109] In addition, in this example, the gas passageway is cooled with cooling water 18 as shown in drawing 8.

[0110] Moreover, in this example, in the inlet-port this side of the distributed section 22, the extension 69 is formed independently and the radiation prevention section 102 of straight side is arranged to this extension. In the gas outlet 7 side of the radiation prevention section, pore 101 was formed and the bore has spread in the shape of a taper toward the carburetor side.

[0111] This extension 69 is also a part for preventing stagnation of the described material gas in an example 3. Of course, it is good also as a configuration unified as it is not necessary to form an extension 69 independently and was shown in <u>drawing 6</u>.

[0112] As an extended include angle theta in an extension 69, 5 - 10 degrees is desirable. When theta is this within the limits, material gas can be supplied to the distributed section, without breaking a turning style. Moreover, when theta is this within the limits, the flow resistance by amplification serves as min, and existence of DEDDO serves as min, and existence of the vortex by existence of the Dead Zone can be recognized min. In addition, as theta, 6 - 7 times is more desirable. In addition, in the case of the example shown in drawing 6, the range of desirable theta is the same.

[0113] (Example 6) Supply of a raw material solution and carrier gas was performed on the conditions which come to rank second using the equipment shown in <u>drawing 8</u>, and the homogeneity in material gas was investigated.

[0114]

The amount of raw-material solution installation: Sr2 (DPM) 0.04 cc/min Bi3 (C6H5) 0.08 cc/min Ta (OC2H5)5 0.08 cc/min THF 0.2 cc/min Carrier gas: Nitrogen gas 10 - 350 m/s [0115] The equipment shown in <u>drawing 8</u> as a vaporizer was used. However, the rod with which the spiral slot is not formed as a rod in the rod shown in <u>drawing 9</u> was used.

[0116] While supplying a raw material solution from the feeding hole 6, various change of the rate was carried out for carrier gas. In addition, from the feeding hole, Ta (OC2H5)5 was supplied to Bi (C6H5)3 and slot 67c, and solvents, such as THF, were supplied to 67d of slots at slot 67a at Sr (DPM)2 and slot 67b, respectively.

[0117] Heating in the evaporation section was not performed but the particle diameter of the raw material solution in the material gas which extracted and extracted material gas in the gas outlet 7 was measured.

[0118] The result is shown in <u>drawing 11</u> as a relative value (the case where the equipment concerning the conventional example shown in <u>drawing 12</u> (a) is used is set to 1). By making the rate of flow into 50 or more m/s, a dispersed particle diameter becomes small and a dispersed particle diameter becomes still smaller by considering as 100 or more m/s so that <u>drawing 11</u> may show. However, a dispersed particle diameter is saturated also as 200m/s or more. Therefore, 100 - 200 m/s is the more desirable range.

[0119] (Example 7) In this example, the rod which formed the spiral slot as a rod was used.

[0120] Other points presupposed that it is the same as that of an example 6.

[0121] The concentration of the raw material solution supplied to the slot in the extension of a slot in the example 6 was deep. namely, -- that is, Sr (DPM)2 had [Bi (C6H5)3] the concentration of the others [Ta/(OC2H5)/5] in the extension of slot 67c high in the extension of slot 67a at the extension of slot 67b respectively.

[0122] However, in every part, each organic metal raw material of the mixed material gas obtained in the edge of a spiral slot in this example was uniform.

[0123] (Example 8) An example 8 is shown in drawing 12 and drawing 13.

[0124] Conventionally, installation of oxygen was performed only on the lower stream of a river of the evaporation section 22, as shown in <u>drawing 2</u>. In the column of a Prior art, it says that carbon contains in the large quantity in the film formed in the Prior art, and it is a passage. Moreover, gap had arisen in the presentation allocation in a raw material, and presentation allocation in the formed film. That is, when membranes were formed by adjusting a raw material to the presentation ratio as a stoichiometric ratio, and evaporating it, the film formed actually had turned into film of the presentation [stoichiometric ratio] shifted. The phenomenon (about 0.1at%) in which \*\*\*\*\*\* content of the bismuth was not carried out especially was observed.

[0125] this invention person found out that this cause was related to the introductory location of oxygen. That is, as shown in <u>drawing 20</u>, when introducing oxygen with carrier gas from a gas inlet 4, the nearest to exhaust nozzle secondary oxygen supply opening 200, and the oxygen inlet (primary oxygen supply opening) 25, it turned out that a gap of the presentation ratio between the presentations in a raw

material solution can make the presentation in the formed film a very small thing.

[0126] In addition, carrier gas and oxygen are mixed beforehand and the mixed gas may be introduced from a gas inlet 4.

[0127] (Example 9) Using <u>drawing 19</u>, the carburetor shown in 20, and the CVD system shown in <u>drawing 21</u>, the SBT film was formed and the polarization property etc. was evaluated further.

[0128] Specifically, the conditions of a carburetor and the conditions of a reaction chamber formed the SBT thin film on the substrate which controlled as follows and formed 200nm of platinum on the silicon substrate which oxidized. concrete -- condition:hexa ethoxy strontium tantalum Sr[Ta(OC2H5)6] 2 0.1 molar solution (solvent: hexane)

0.02ml/min.

Tree t-friend ROKISHIDO bismuth Bi3 (O-t-C5H11) 0.2 molar solution (solvent: hexane) 0.02 ml/min

The first carrier Ar=200sccm (it puts in from a gas inlet 4) The first carrier O2= 10sccm (it puts in from a gas inlet 4)

The 2nd carrier Ar= 20sccm (it puts in from a gas inlet 200)

O2= 10sccm (it puts in from a gas inlet 200)

Reaction oxygen O2=200sccm (it puts in from the distributed blowout section lower part 25)

Reaction oxygen temperature 216 degrees C (it is the heater separately formed before putting in from the distributed blowout section lower part, and is temperature control)

Wafer temperature 475-degree-C space temperature 299-degree-C air clearance 30mm shower head temperature reaction pressure of 201 degrees C 1 Torr membrane formation time amount As a result, it is SBT film thickness 20 part. About 300nm (rate-of-sedimentation about 150nm/min.)

```
SBT組成 Sr 5. 4 at%
Bi 16. 4 at%
Ta 13. 1 at%
O 61. 4 at%
C 3. 5 at%
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The presentation in the formed film of a gap of the presentation ratio between the presentations in a raw material solution is small, and the rate of sedimentation is also the conventional ratio. It increased about 5 times. It turns out that the effectiveness which introduces a small amount of oxygen with carrier gas from a gas inlet 4 is very large. There are also few carbon contents as 3.5at(s)%.

[0129] Before putting in reaction oxygen 200 cc/min. from the distributed blowout section lower part, it temperature-control(216 degrees C)-wrote to accuracy at the heater formed separately, and that the effectiveness which controls the re-condensation and sublimation of an organometallic compound (solidification) which evaporated is large has checked from the dirt of the vaporizing tube lower part having been lost.

[0130] 750 degrees C and crystallization processing for 30 minutes were performed in the oxygen ambient atmosphere after this SBT thin film formation, and the place which formed the up electrode and carried out measurement assessment, the outstanding crystallization property, and the polarization property were shown. This <u>Drawing 17</u>, 18 It was shown.

[0131] It is [from / as shown in drawing 2], when introducing oxygen simultaneously on the lower stream of a river of the evaporation section, and controlling the amount of oxygen suitably makes gap of a presentation ratio small more and it decreases a carbon content] desirable if only it introduces oxidizing gases, such as oxygen, from a gas inlet 4 or primary oxygen supply opening of the nearest to an exhaust nozzle.

[0132] The content of the carbon in the formed film can be decreased to 5% - 20 conventional%. [0133] The example of a SBT thin film deposition process is explained using <u>drawing 20</u>. An aperture and a bulb 1 are closed for a bulb 2, a reaction chamber is lengthened to a high vacuum, and a wafer is transferred to a reaction chamber from a load lock chamber after several minutes. At this time In a carburetor, it is hexa ethoxy strontium tantalum Sr[Ta(OC2H5)6] 2. 0.1 molar solution (solvent: hexane)

0.02ml/min.

Tree t-friend ROKISHIDO bismuth Bi3 (O-t-C5H11) 0.2 molar solution (solvent: hexane) 0.02 ml/min The first carrier Ar=200sccm (it puts in from a gas inlet 4)

The first carrier O2= 10sccm (it puts in from a gas inlet 4) is flowing, and it lengthens via the bulb 2 and the pressure automatic regulating valve to the vacuum pump. At this time, a pressure gage is controlled by the pressure automatic regulating valve by 4Torr. If a wafer is transferred and temperature is stabilized after several minutes, an aperture and a bulb 2 will be closed for a bulb 1, the following gas will be passed to a reaction chamber, and deposition will be started.

Hexa ethoxy strontium tantalum Sr [Ta (OC2H5)6] 2 0.1 molar solution (solvent: hexane) 0.02ml/min.

Tree t-friend ROKISHIDO bismuth Bi3 (O-t-C5H11) 0.2 molar solution (solvent: hexane) 0.02 ml/min

The first carrier Ar=200sccm (it puts in from a gas inlet 4)

The first carrier O2= 10sccm (it puts in from a gas inlet 4)

The 2nd carrier Ar= 20sccm (it puts in from a gas inlet 200)

O2= 10sccm (it puts in from a gas inlet 200)

Reaction oxygen O2=200sccm (it puts in from the distributed blowout section lower part 25)

Reaction oxygen temperature 216 degrees C (it is the heater separately formed before putting in from the distributed blowout section lower part, and is temperature control)

Wafer temperature 475-degree-C reaction pressure chamber pressure is controlled to 1Torr.

(It is based on the pressure automatic regulating valve which is not indicated)

If predetermined time amount (here 20 minutes) passes, an aperture and a bulb 1 will be closed for a bulb 2, and deposition will be ended. A reaction chamber is lengthened to a high vacuum, reactant gas is removed thoroughly, and a wafer is taken out to a load lock chamber after 1 minute.

Capacitor structure Pt(200nm)/CVDSBT(300nm)/Pt(175nm)/Ti(30nm)/SiO2/Si capacitor creation process lower electrode formation Pt (175nm)/TI (30nm) CVDSBT film formation (300nm) SBT film crystallization processing (diffusion-furnace annealing: wafer 750degree C, 30min, O2

ambient atmosphere)

Up electrode formation Pt (200nm)

Annealing: 650 degrees C, O2, 30min [0134] Former Reaction oxygen (example.) 200sccm(s) were in the room temperature condition, since it was putting into the vaporizing tube, it was cooled, and organic metal gas had adhered and deposited them at the vaporizing tube. When temperature control of the reaction oxygen supplied from the evaporation section lower part was performed, conventionally, the heater was twisted around the exterior of stainless steel tubing (1 / 4-1/16 inch appearance, ten to 100 cm die length), and temperature of a stainless steel tubing outer wall was controlled (example: 219 degrees C).

[0135] Temperature of a stainless steel tubing outer wall (example: 219 degrees C) = the interior was considered to be the temperature of the flowing oxygen (flow rate 200sccm), and it was.

[0136] However, when measuring oxygen temperature by the detailed heat conductive pair, in the above-mentioned example, temperature up was not carried out to about 35 degrees C.

[0137] Then, the oxygen temperature after heating was measured by the directly detailed heat conductive pair, heating heater temperature was controlled, and oxygen temperature was controlled to accuracy. It was not easy to carry out temperature up of the gas, such as oxygen which flows tubing, and it put in packing in the heating tube, aimed at improvement in heat exchange effectiveness, measured the heated oxygen gas temperature, and controlled heating heater temperature proper. The means for this control is the heat exchanger shown in drawing 20.

[0138] (Example 10) An example 10 is shown in drawing 14.

[0139] Although the raw material solution which atomized said example by spraying gas on each of a single raw material solution, and was atomized after that was mixed, this example mixes two or more raw material solutions, and, subsequently is equipment for atomizing a mixed raw material solution. [0140] Two or more solution paths 130a and 130b to which this example supplies the raw material

solutions 5a and 5b, The mixed section 109 which mixes two or more raw material solutions 5a and 5b supplied from two or more solution paths 130a and 130b, [ in the supply path 110 which has the outlet 017 where an end is open for free passage in the mixed section 109, and becomes the evaporation section 22 side, and the supply path 110 ] In the mixed raw material solution which came out of the mixed section 109, carrier gas Or the gas passageway 120 arranged so that the mixed gas of carrier gas and oxygen may be sprayed, The distributed machine 150 with which the cooling means for cooling the inside of the supply path 110 is formed, The vaporizing tube by which the end was connected to the coil of an MOCVD system and the other end was connected to the outlet 107 of the distributed machine 150, The radiant heat prevention material 102 which has the heating means 2 for heating a vaporizing tube, has the evaporation section 22 for making the gas containing the raw material solution sent from said distributed machine 150 heat and evaporate, and has pore 101 on the outside of an outlet 107 is arranged.

[0141] In this example, it is effective in the raw material solution with which a reaction does not advance even if it mixes, and in order to once atomize after mixing, compared with the case where it mixes after atomization, a presentation serves as accuracy. Moreover, the means (not shown) for analyzing the presentation of the mixed raw material solution in the mixed section 109 is established, and if the amount of supply of the raw material solutions 5a and 5b is controlled based on an analysis result, it will become possible to acquire a much more exact presentation.

[0142] Moreover, in this example, since it is not necessary to use a rod (10 of <u>drawing 1</u>), it is not said that the heat which spread the rod heats the inside of the supply path 110. Furthermore, since the cross section of the supply path 110 can be made small compared with the case where it mixes after atomization, as a result the cross section of an outlet 107 can be made small, it is also rare to heat the inside of the supply path 110 by radiation. Therefore, the radiation prevention section 102 cannot be formed but \*\* can also lessen a deposit of a crystal etc. However, as shown in <u>drawing 14</u>, the radiation prevention section 102 may be formed to prevent a deposit of a crystal etc. further.

[0143] In addition, in the above example, although pore showed one example, of course, plural is sufficient as it. Moreover, as a path of pore, 2mm or less is desirable. When preparing more than one, considering as a still smaller path is also possible.

[0144] Moreover, in the above example, when carrier passage and a raw material solution inlet are acute angles (30 degrees), a solution is lengthened by gas. A solution will be pushed on gas if it is 90 degrees or more. Therefore, 30-90 degrees is desirable. Specifically, the optimal include angle is decided from the viscosity and the flow rate of a solution. When viscosity is large, or when a flow rate is large, by making it an acute angle more, a solution flows smoothly. Therefore, what is necessary is just to ask for the optimal include angle corresponding to viscosity and a flow rate by experiment etc. beforehand, if in charge of operation.

[0145] Moreover, in the above example, it is desirable to establish the device for controlling the distance of the space between the shower head and a susceptor in the distance of arbitration.

[0146] Furthermore, while forming the liquid massflow controller for controlling the flow rate of a raw material solution, it is desirable to establish the deaeration means for deaerating to the upstream of this liquid massflow controller. It does not deaerate but dispersion in the film formed when the raw material solution was introduced into the massflow controller arises on the same wafer or between other wafers. Dispersion in the above-mentioned thickness decreases remarkably by introducing a raw material solution into a massflow controller, after deaerating helium etc.

[0147] Dispersion in thickness can be further prevented by establishing the means for controlling a raw material solution, a helium feeding container, a liquid massflow controller, and the temperature of piping [ before and after ] to constant temperature. Moreover, deterioration of an unstable raw material solution can also be prevented chemically. In case a SBT thin film is formed, it is the range of 5 degrees C - 20 degrees C, and controls to a precision. 12 degrees C especially \*\*1 degree C is desirable. [0148] Moreover, it sets to the substrate surface treatment equipment which performs predetermined gas to substrate front faces, such as drawing 22 and a silicon substrate as shown in 23, and performs surface treatment to a blasting this substrate front face. The upper ring 301 connected with the heat carrier inlet

port 320 for percolation of a heat carrier, The down-stream ring 302 connected with the heat carrier outlet 321 of said predetermined heat carrier, At least two heat transfer way 303a which connects mutually between said upper rings 1 and down-stream rings 2 in parallel, and forms the passage of said heat carrier, It is desirable that the heat carrier circuit for having 303b, making the direction of passage from said upper ring 1 to the down-stream ring 302 between said adjoining heat transfer way 303a and 303b into alternation, and making said gas into predetermined temperature should be constituted.

[0149] Moreover, said substrate surface treatment equipment is in the predetermined flat surface in said heat carrier circuit, and it is still more desirable to make it possible to have the thermal-conversion plate 304 thermally connected with said heat carrier circuit into the flat surface in which the passage of said said parallel heat carrier was formed, and to heat the inside of said flat surface of this thermal-conversion plate 304 to abbreviation homogeneity temperature with said heat carrier.

[0150] Furthermore, it is desirable to make it possible to heat said predetermined gas which two or more air holes which pass said predetermined gas to the perpendicular direction of this flat surface are formed in said flat surface of said thermal-conversion plate 304, and passes this air hole to abbreviation homogeneity temperature in said flat surface.

[0151] Thereby, the direction of passage from an upper ring to the down-stream ring between the heat transfer ways where a heat carrier circuit adjoins is constituted as alternation. for this reason, the temperature gradient of the field contiguous to a heat transfer way -- high / low / high / low ones -- it is constituted with .... This configuration enables it to heat or cool a thermal-conversion plate to homogeneity. Furthermore, it has the thermal-conversion plate thermally connected with the heat carrier circuit into the flat surface in which the passage of a parallel heat carrier was formed. Therefore, it becomes possible about heating the inside of the flat surface of this thermal-conversion plate to abbreviation homogeneity temperature with a heat carrier.

[0152] (Example 11) The example of an improvement of a SBT thin film deposition process is shown using drawing 24. An aperture and bulb 208V1 are closed for bulb 206V2, a reaction chamber (process room) 203 is lengthened to a high vacuum, and a wafer is transferred to a reaction chamber 203 from the load lock chamber 204 after 1 minute.

[0153] At this time, the following raw material is flowing to the carburetor (evaporation room) 205. Hexa ethoxy strontium tantalum Sr [Ta (OC2H5)6] 2 0.004 molar solution (solvent: hexane) 0.50ml/min.

Tree t-friend ROKISHIDO bismuth Bi(O-t-C5H11)30.008 molar solution (solvent: hexane) 0.50 ml/min

The first carrier Ar=200sccm (it puts in from a gas inlet 4)

The first carrier O2= 10sccm (it puts in from a gas inlet 4)

The raw material is exhausted to the vacuum pump via bulb 206V2 and the pressure automatic regulating valve 207. At this time A pressure gage is 4Torr by the pressure automatic regulating valve. It is controlled. If a wafer is transferred and temperature is stabilized after 4 minutes, an aperture and bulb 206V2 will be closed for bulb 208V1, the following gas will be passed to a reaction chamber 203, and deposition will be started.

Hexa ethoxy strontium tantalum Sr [Ta (OC2H5)6] 2 0.004 molar solution (solvent: hexane) 0.50ml/min.

Tree t-friend ROKISHIDO bismuth Bi(O-t-C5H11)30.2 molar solution (solvent: hexane) 0.50 ml/min

The first carrier Ar=200sccm (it puts in from a gas inlet 4)

The first carrier O2= 10sccm (it puts in from a gas inlet 4)

The 2nd carrier Ar= 20sccm (it puts in from a gas inlet 200)

O2= 10sccm (reaction oxygen O2=200sccm (it puts in from the distributed blowout section lower part 25) put in from a gas inlet 200)

Reaction oxygen temperature 216 degrees C (it is the heater separately formed before putting in from the distributed blowout section lower part, and is temperature control)

Wafer temperature 475-degree-C reaction pressure chamber pressure is controlled to 1Torr. (It is based on the pressure automatic regulating valve which is not indicated)

If predetermined time amount (here for example, 20 minutes) passes, an aperture and bulb 208V1 will be closed for bulb 206V2, and deposition will be ended. The SBT thin film with a thickness of about 200nm accumulated. A reaction chamber 203 is lengthened to a high vacuum, reactant gas is removed thoroughly, and a wafer is taken out to the load lock chamber 204 after 1 minute. Next, a new wafer is carried, after 4 minutes, closing and bulb 208V1 are opened for bulb 206V2, and deposition is started. Although there is time amount for about 5 minutes until it ends deposition and deposition of the following wafer is started, a carburetor 205 is cleaned in this case. It is hexa ethoxy strontium tantalum Sr[Ta(OC2H5)6] 2 promptly after deposition termination. 0.004 molar solution (solvent: hexane) Tree t-friend ROKISHIDO bismuth A high grade hexane is passed to Bi(O-t-C5H11) 30.008 molar-solution (solvent: hexane) MFC. Flow rate a total of 1.0-/min. Time amount is for 3 minutes. When 3 minutes pass, it is hexa ethoxy strontium tantalum Sr[Ta(OC2H5)6] 2 again. 0.004 molar solution (solvent: hexane)

Tree t-friend ROKISHIDO bismuth Bi(O-t-C5H11)30.008 molar solution (solvent: hexane) It is alike and changes.

[0154] 2 minutes after changing Again Deposition of a SBT thin film is started. Since piping capacity was 1.2 cc, it was able to approach the above-mentioned actuation and was able to clean the carburetor. After repeating this actuation 20 times, when the carburetor was disassembled and checked, there was no dirt of a carburetor, especially a atomization nozzle part.

[0155] (Example 12) The example of an improvement of a SBT thin film deposition process is shown using <u>drawing 25</u>.

[0156] An aperture and bulb 208V1 are closed for bulb 206V2, a reaction chamber 203 is lengthened to a high vacuum, and a wafer is transferred to a reaction chamber 203 from the load lock chamber 204 after 1 minute. At this time In a carburetor 205, it is hexa ethoxy strontium tantalum Sr[Ta(OC2H5)6] 2. 0.004 molar solution (solvent: hexane)

0.50ml/min.

Tree t-friend ROKISHIDO bismuth Bi(O-t-C5H11)30.008 molar solution (solvent: hexane) 0.60 ml/min

The first carrier Ar=200sccm (it puts in from a gas inlet 4)

The first carrier O2= 10sccm (it puts in from a gas inlet 4)

It lengthens to the vacuum pump via \*\*\*\*\*\*\*\*\*, bulb 206V2, and the pressure automatic regulating valve 207. At this time A pressure gage is 4Torr by the pressure automatic regulating valve. It is controlled. If a wafer is transferred and temperature is stabilized after 4 minutes, an aperture and bulb 206V2 will be closed for bulb 208V1, the following gas will be passed to a reaction chamber 203, and deposition will be started.

Hexa ethoxy strontium tantalum Sr [Ta (OC2H5)6] 2 0.004 molar solution (solvent: hexane) 0.50 ml/min

Tree t-friend ROKISHIDO bismuth Bi(O-t-C5H11)30.2 molar solution (solvent: hexane) 0.60 ml/min The first carrier Ar=200sccm (it puts in from a gas inlet 4)

The first carrier O2= 10sccm (it puts in from a gas inlet 4)

The 2nd carrier Ar= 20sccm (it puts in from a gas inlet 200)

O2= 10sccm (reaction oxygen O2=200sccm (it puts in from the distributed blowout section lower part 25) put in from a gas inlet 200)

Reaction oxygen temperature 216 degrees C (it is the heater separately formed before putting in from the distributed blowout section lower part, and is temperature control)

Wafer temperature 475-degree-C reaction pressure chamber pressure is controlled to 1Torr. (It is based on the pressure automatic regulating valve which is not indicated)

If for 1 minute passes, an aperture and bulb 208V1 will be closed for bulb 206V2, and deposition will be ended.

[0157] Next, a flow rate is changed.

Hexa ethoxy strontium tantalum Sr[Ta(OC2H5)6] 20.004 molar-solution (solvent: hexane) 0.50 ml/min Tree t-friend ROKISHIDO bismuth Bi(O-t-C5H11)30.2 molar solution (solvent: hexane) 0.50 ml/min

An aperture and bulb 206V2 are closed for bulb 208V1 after 1 minute, and deposition is resumed. An aperture and bulb 208V1 are closed for bulb 206V2 after progress for 7 minutes, and deposition is ended. The SBT thin film with a thickness of about 80nm accumulated. A reaction chamber 203 is lengthened to a high vacuum, reactant gas is removed thoroughly, and a wafer is taken out to the load lock chamber 205 after 1 minute. Next, a new wafer is carried, after 4 minutes, closing and bulb 208V1 are opened for bulb 206V2, and deposition is started.

[Effect of the Invention] 1. Although the globule adhered at the head of a carburetor conventionally and blinding was produced by operation of 5 hours, in this invention, blinding etc. cannot be started and the carburetors for membrane formation equipment and other equipments for [ in which a long-term activity is possible and / in which the stable feeding to the reaction section is possible ] MOCVD can be offered. [0159] 2. The presentation of a CVD thin film can be changed and controlled in the thickness direction.

[0160] 3. Lowering of cost can be aimed at.

[0161] 4. Lowering of the rate of sedimentation and DEPORETO can be lost.

[Translation done.]